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Raw and acetylated Sugarcane Bagasse *(Saccharum officinarum)* and Rubber wood *(Hevea brasiliensis)* in oil spill sorption at Pantai Kuala Perlis

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Raw and acetylated Sugarcane Bagasse (*Saccharum officinarum*) and Rubber wood (*Hevea brasiliensis*) in oil spill sorption at Pantai Kuala Perlis

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Abstract. In this research, raw and modified (acetylated) sugarcane bagasse (SGB) (*Saccharum officinarum*) and rubber wood (RB) (*Hevea brasiliensis)* were used as sorbents in oil sorption to absorb the used oil in the seawater sample at Pantai Kuala Perlis. The research is done using different time which are 5, 10 and 15 minutes with different thickness of oil layer which are 10 and 20 ml, using 2 g of sorbents. In the percentage of oil removal and oil sorption capacity, 15 minutes was chosen as optimum adsorption time and 10 ml as optimum oil thickness. In term of effect of adsorption time, for overall results, the longer the adsorption time, the higher the sorption capacity and percentage removal of oil. Meanwhile, in term of effect of oil layer thickness, the lower the thickness of oil layer, the higher the sorption capacity and percentage removal. For Fourier Transform Infrared Spectroscopy (FTIR), the spectroscopic data shown that both modified SGB and RB had O-H, CH_3 and C=O functional group at the range of 3000-3500, 2500-3000 and 1500-2000 cm-^{1} respectively. These shown that modified RGB and RB had successfully synthesized. For salinity test, there were no significance different between the initial salinity and after-adsorption salinity of the seawater sample.

1. Introduction

Oil pollution in marine environment is one of the major concerns for several countries with rapid industrials. The oil pollution has steadily increased as oil consumption has increased. It can lead to the destruction of aquatic biodiversity and also the rest of the earth. The unpleasant odor from the spilled oil can affect the economy and tourism of the countries. Protection of water sources must therefore be one of the major issues in our lives and action should be taken to remove these pollutants because we really need water in our lives (Behnood R. et al., 2016). Oil spill pollution is always have been a serious problem in aquatic environment that continuously growing every year. This type of pollution has long-term effects on biosphere. Oil and fuel runoff from land based sources, unintended spills from tankers, and oil drilling mishaps are the biggest sources of oil pollution in the ocean and other watercourses (Fingas, 2001). Therefore, unless it is removed as quickly as possible, spilled oil causes huge environmental problems and disaster. It will lead to oil waste contaminant in ocean. This study was designed to investigate the effectiveness of using raw and modified sugarcane bagasse and rubber wood as adsorbent in separation of oil and seawater. The parameters of this study were the application of sugarcane bagasse (SCB) and rubber wood (RW). Raw and modified sugarcane bagasse and rubber wood (acetylated) were used as adsorbent in the separation of oil and a seawater sample because they can give different results. It was because different wood or bagasse will give different results in the oil sorption capacity. Approximately two hundred variety of sorbent materials are being produced and used these days. Sorbents can be split up into certain basic groups which are inorganic, organic, natural, organo-mineral and synthetic. The natural fiber products, straw, grain crops hull, processed flax waste, sawdust and peat used as sorbents mostly are used as natural sorbents. Cellulose is one of particular importance as among the important structural components of plant materials (Olga R. et al., 2014). Thus the organic sorbents are the most widely used natural sorbents due to their oleophilic and hydrophobic qualities, synthetic materials including the polypropylene and polyurethane (C. Karan et al., 2011). Furthermore, developing an adsorbent showing high adsorption capacity and low cost to remove various pollutants from contaminated waters was particularly interesting. Inorganic adsorbents such as coal, clays, clay minerals and adsorbents of zeolites have been widely studied to provide an alternative to activated carbon in the treatment of surface and soil water and industrial wastewater (S. Babel TA & Kurniawan et al., 2003). Rubber wood and sugarcane baggase were choose as a natural adsorbent in this study. Based on centralized experience, rubber wood has capability for other value-added applications in Southeast Asia (de Jesus Eufrade Junior et al., 2015).

2. Materials and methods

2.1 Preparation of raw bagasse and wood

The fresh sugarcane bagasse (SGB) and rubber wood (RB) first were washed and cleansed with the tap water and also distilled water to eliminate dust and then dry in open air. Then, it was grinded using the industrial grinder into smaller sizes. There will be two sizes which were 10 and 30 mesh sizes. After that, the grinded SGB and RB were dried in oven for 24 hours or one day with the temperature of 60°C - 80°C to remove the moisture inside SGB and RB.

2.2 Acetylated bagasse and wood synthesize

Organic sorbents are modified to improve their sorption capacity by chemical reactions. In order to boost the hydrophobic and oleophilic properties of the sorbents for oil spill cleanup, under mild conditions, raw SGB and RB were modified by acetic acid reaction using a catalyst named *N*-bromosuccinimide (NBS). (Onwuka, J.C. et al., 2018). Raw SGB and RB were cleaned with tap and distilled water and then oven-dry for 16 hours with the temperature of 80°C. The substrate and reactant amount were mixed in 1:20 (g sorbent/mL acetic acid) ratio. Then, a portion of sorbent were put in a conical flask of 250 mL contained of 60 mL acetic acid and 0.6 g, which is 1% of the solvent of catalyst, *N*-bromosuccinimide (NBS). The flask was the placed in a temperature-controlled water bath for 90 min which was set at 70 °C, under the atmospheric pressure. The conical flask then was removed from the water bath and the hot reagent was poured out. To eliminate the unreacted by-product acetic acid, the products are thoroughly cleaned with ethanol and acetone. The products were allowed to dry in a 16-hour oven set at 60 ° C and then cooled in a desiccator and placed in reagent bottle prior to the experimental process later.

2.3 Characterization analysis

FTIR and salinity test are used in characterization of the raw and modified SGB and RB. For, the sample of raw and modified SGB and RB are analyze for their fibers surface images. While for FTIR, the chemical structure and functional group of raw and modified SGB and RB were analyze. Last but not least, the salinity test were carried out to measure the effect of salinity on the seawater sample before and after the adsorption test.

2.4 Adsorption experiment

In the oil layer sorption, the seawater sample is measured into 150 mL and put in 500 mL beaker. The used vegetable oil was added into the beaker with different thickness which to form an oil layer. The thickness specified were 10 mL (4 mm) and 20 mL (6 mm). Then, a portion of sorbents which was 2 g were spread over the surface. The time for the adsorption test were set at 5, 10 and 15 minutes. After the sorption time, the sorbent were removed with a strainer that is hanged over the beaker to prevent the oil that are not absorbed from falling down. Then, the residue of oil and the oil-absorbed sorbents were removed from the beaker and the weight were recorded. The percentage removal of oil and oil sorption capacity were calculated using these equation;

Percentage removal of oil (%) = [(Ci - Cf) / Ci] x 100
Ci = Initial weight of oil remained (mL)
Cf = Final weight of oil remained (mL) ……..……..………..…..................................(1)

Oil Sorption Capacity (g/g) = (Sst – So) / So
Sst = Initial mass of dry sorbent (g)
So = Mass of oil-absorbed sorbent at the end of sorption test ……………………..………..(2)

3. Result and discussion

Two parameter were discussed which are adsorption time and thickness of oil layer. The dosage of sorbents was constant throughout the adsorption test which is 2 g.

3.1 Percentage removal of oil

As seen in Figure 1 and 2, the percentage removal of oil in sugarcane bagasse (SGB) and rubber wood (RB) in two conditions which are raw and acetylated, were calculated using these formula; Percentage removal of oil (%) = [(Ci - Cf) / Ci] x 100
Ci = Initial weight of oil remained (mL)
Cf = Final weight of oil remained (mL)

3.1.1. Effect of adsorption time in percentage removal

Figure 1 showed the percentage removal of oil with 10 mL thickness of oil with 2 g of sorbents. Looking at the graph, it was find out that at 5 minutes reaction, raw and acetylated SGB shown the same percentage removal of oil which is 12.5 %. And as the time increase to 10 minutes to 15 minutes, the graph showed increasing steadily. Then, for rubber wood, it shown that raw RB is having 37.5 % removal of oil compared to the acetylated which is 42.5 %. Next, after increasing the time to 10 minutes, acetylated RB having same percentage at 42.5 % but not for raw, it increasing sharply to 50%. However, raw RB is decreasing to 37.5 % at 15 minutes of adsorption. So it can be conclude that both acetylated are effective at 15 minutes reactions because it showed the increasing pattern. And it can also be conclude that wood (RB) show highest percentage compared to non-wood (SGB). So it can be decided that 15 minutes as the optimum time for both acetylated RB and SGB. Figure 2 showed the percentage removal of oil at 15 minutes with different thickness of oil with 2 g of sorbents. From the bar graph above at 10 ml, raw SGB had the least percentage removal which is 25 % compared to the other three sorbents. Meanwhile, the highest percentage removal was acetylated RB which is 45 %. Next, at 20 ml, raw SGB,

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acetylated SGB and acetylated RB had almost same percentage oil removal which is 35 %, 35.35 % and 35.35 % respectively. And for raw RB, it had the least percentage oil removal which is 25 %. In comparison of the two different thicknesses, raw and acetylated SGB had increasing pattern of the percentage oil removal from 10 ml to 20 ml, which are from 25 % to 35 % and 30 % to 35.35 % respectively. However, raw and acetylated RB had decreasing patter from 35.7 % to 25 % and 45 % to 35.35 % respectively.

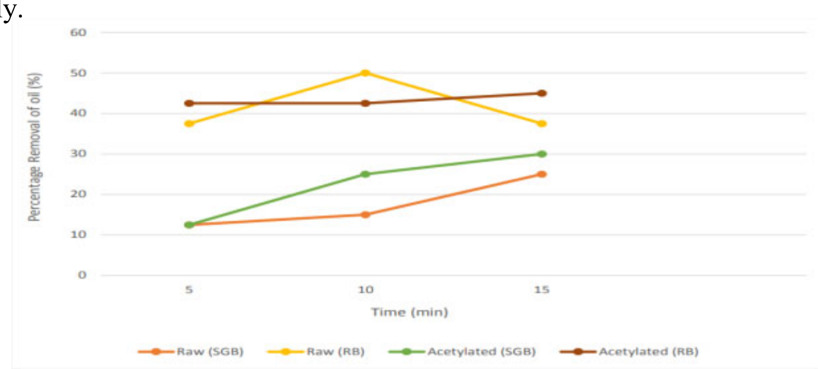

Figure 1. Percentage oil removal of oil of 10 mL for 2 g of raw SGB, acetylated SGB, raw RB and acetylated RB

Therefore, we can conclude that 10 ml is an effective oil thickness because the percentage oil removal of the sorbents was mostly higher than 20 ml. Besides, we can also conclude that the nonwood (SGB) had higher percentage than wood (RB). So, we decided to choose 10 ml as the optimum thickness of oil in the percentage oil removal. The rubber wood is a diffuse- porous end grain and also has large to very large pores. (E. Meier, 2008). It can be assume that the large pores and the diffuse-porous of RB might be the main reason in higher percentage removal of oil in different thickness of oil layer.

Effect of Thickness of oil in percentage removal

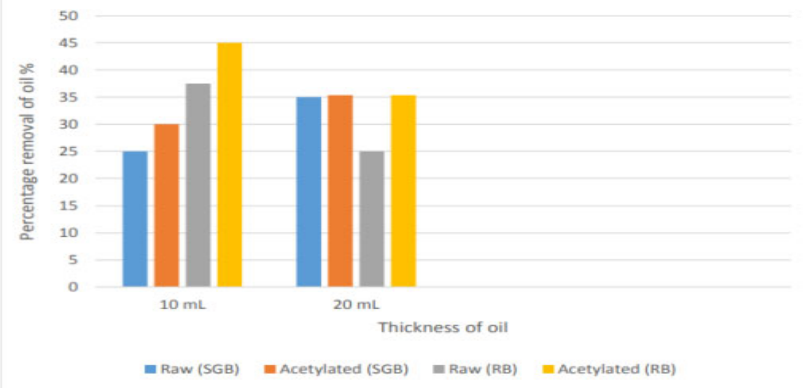

Figure 2. Percentage oil removal of 2 g of raw SGB, acetylated SGB, raw RB and acetylated RB, at 15 minutes absorption with different thickness of oil

3.2. Oil sorption capacity

Figure 3 shows that the oil sorption capacity in sugarcane bagasse (SGB) and rubber wood (RB) in two conditions which are raw and acetylated, were calculated using these formula;

Oil Sorption Capacity (g/g) = (Sst – So) / So

Sst = Initial mass of dry sorbent (g)

So = Mass of oil-absorbed sorbent at the end of sorption test.

Figure 3 showed the oil sorption capacity with 10 ml thickness of oil with 2 g of sorbents. When we look at the graph, we find out that at 5 minutes reaction, raw SGB start at the highest oil sorption capacity which is 5.595 g/g compared to other sorbents. And as we increase the time to 10 minutes and 15 minutes, the graph increased steadily. However, as for acetylated SGB, at 5 minutes, it start at 4.080 g/g of oil sorption capacity and the graph start to slightly decrease at 10 minutes, having 3.265 g/g of oil sorption capacity. Then at 15 minutes, it slightly became increased to 3.968 g/g. Next, same goes to the graph pattern of raw and acetylated RB. As for raw RB, at 5 minutes mark, the oil sorption capacity is 3.825 g/g, and then it declined gradually before it slightly rose up to 3.660 g/g at 15 minutes of adsorption.

3.2.1. Effect of adsorption time in oil sorption capacity

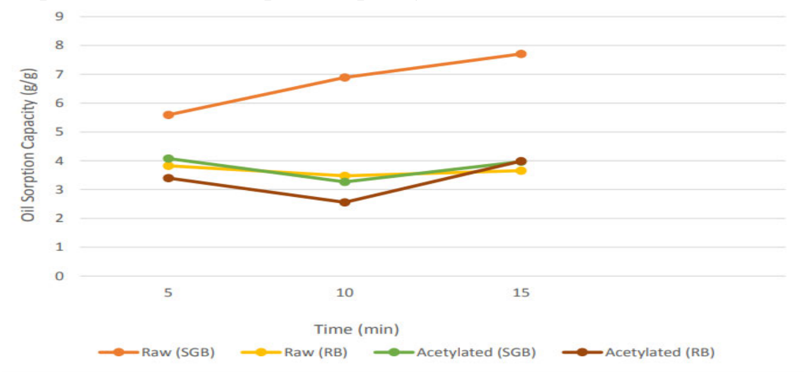

Figure 3. Oil sorption capacity of 10 mL for 2 g of raw SGB, acetylated SGB, raw RB and acetylated RB

So, we can concluded that all sorbents were very effective at 15 minutes of adsorption time. In adsorption time, time is very important for oil to be absorbed into the sugarcane bagasse and rubber wood. If it does not have enough time for the oil to be absorb by sorbents, the sorption capacity will be low. Besides, if there is too much time given to the sorbents, it may cause surface damages to the structure of the sugarcane bagasse and rubber wood fiber. Then, the oil will be disperse out from the sorbent's fiber, making the sorption capacity become low. This may be due to adsorption on first surface and then start to penetrate the inner microscopic voids. (Hussain et al., 2008).

3.2.2 Effect of the thickness of oil layer in oil sorption capacity

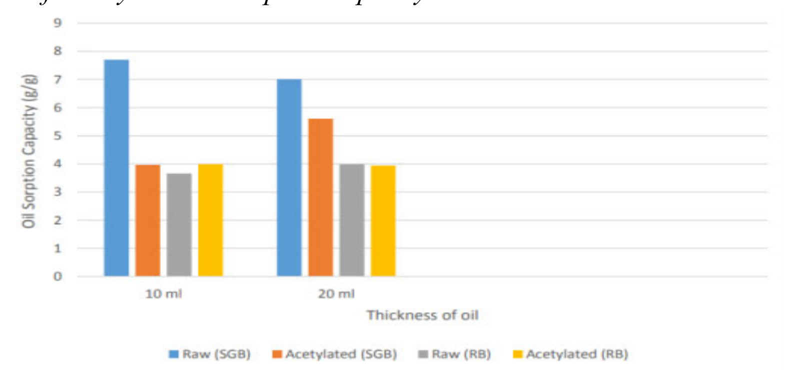

Figure 4. Oil sorption capacity of 2 g of raw SGB, acetylated SGB, raw RB and acetylated RB, at 15 minutes absorption with different thickness of oil

Figure 4 showed the oil sorption capacity with different thickness of oil with 2 g of sorbents at 15 minutes. At 10 ml, raw SGB recorded the highest capacity which is 7.705 g/g compared to other three sorbents. While for acetylated SGB, raw RB and acetylated RB had almost the same capacity which are 3.968 g/g, 3.660 g/g and 3.989 g/g respectively. Moreover, as for 20 ml, raw SGB also recorded the highest capacity of 7.012 g/g. And the capacity of acetylated SGB recorded the next highest capacity which is 5.609 g/g. Meanwhile, raw and acetylated RB had almost the same capacity which are 3.993 g/g and 3.942 g/g respectively. As for the comparison between the two different thicknesses, the graph of raw SGB slightly dropped at 10 ml to 20 ml which is from 7.705 g/g to 7.012 g/g despite having the highest capacity. Next, acetylated SGB increased gradually from 3.968 g/g to 5.609 g/g. Same goes to the raw RB, which has slightly increasing pattern, but not for acetylated RB. Acetylated RB slightly decreased its capacity from 3.989 g/g to 3.942 g/g. So, we can concluded that the non-wood (SGB) especially raw, had better oil sorption capacity compared to wood (RB). Therefore, we decided to choose 10 ml as the optimum thickness of oil in the oil sorption capacity.

3.3. FTIR analysis

To analyse the functional groups in between the two sorbents which are modified sugarcane bagasse (SGB) and rubber wood (RB), Figure 5 shows the FTIR spectrum of modified SGB, before and after oil sorption. At wavenumber of 3000 – 3500 cm^{-1}, the presence of O-H is shown on the graph before and after the oil sorption. The peak attributed to the stretching vibrations of hydroxyl groups present in cellulose, hemicellulose, and the lignin of sugarcane bagasse. (R. Behnood et al., 2016).

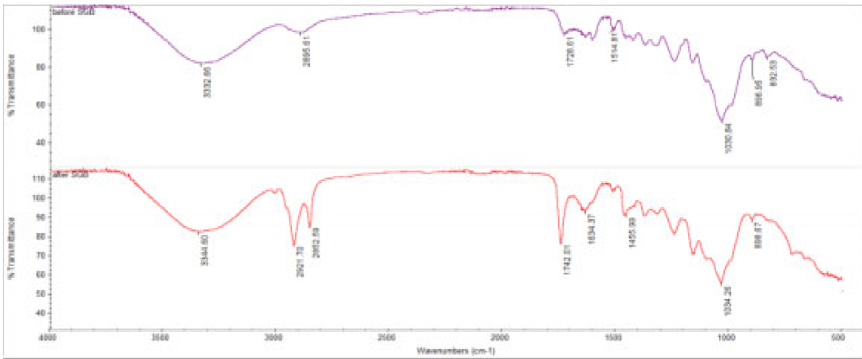

Figure 5. FTIR analysis of before and after oil sorption of modified sugarcane bagasse (SGB)

There were also increasing change of band in the range of 2895.61 till 2921.70 cm^{-1} which represent CH_3 stretching. Before oil sorption, the band only had one peak, then it changed to two peak at after oil sorption. Besides, there were also increasing peak from before to after oil sorption at the range of 1500 till 2000 cm-1 which was from 1728.61 cm-1 to 1742.01 cm^{-1}. The peak represent the carbonyl group which is C=O ester. (R.Behnood et al., 2016). Moreover, at the range of 1030.84 - 1034.26 cm^{-1}, there are also change of band that represent CH_3. There are mostly peaks that represent the CH_3 stretching, which indicate that acetic acid were present in the modified SGB. Figure 6 shows the FTIR spectrum of modified RB, before and after oil sorption. The wavenumber range at 3333.16–3324.45 cm^{-1} has increasing change of band.

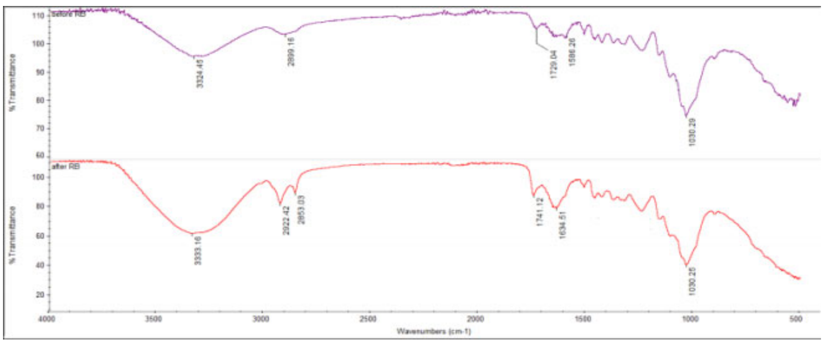

Figure 6. FTIR analysis of before and after oil sorption of modified rubber wood (RB)

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From the research before, the peak in the region of 3000-3500 cm^{-1} represents the stretching of hydroxyl groups. Next, the increasing number of peak from 2899.16 cm^{-1} , which is at before oil sorption after oil sorption at 2922.42 cm-1 and 2853.03 cm^{-1}, represent CH_3. It indicates that the modification of RB with acetic acid were successful. Furthermore, there are also increasing peak at the range of 1586.26-1634.51 cm^{-1} which indicates the presence of C=O stretching. Meanwhile at the wavenumber range between 1030.29 - 1030.25 cm^{-1}, the peaks represent CH_3. For salinity analysis, handheld salinity meter is used to measure the salinity of the seawater sample. The initial and the after-sorption salinity of seawater sample were measured. It is to study whether the adsorption test affected the salinity of the seawater. For the results, the initial salinity of the seawater sample is 17.6 ppt and the after-sorption is also 17.6 ppt. There are no significance difference at all in the initial and after-sorption of the salinity of the seawater in this study. This shows that adsorption test or activity does not have any effect to the salinity of seawater.

4. Conclusion

From the experiment, raw and acetylated rubber wood was studied in this experiment to examine their oil sorption properties and to be compared to sugarcane bagasse. We can see that rubber wood had the potential as oil sorbent along with the sugarcane bagasse as waste material, which is the certified oil sorbent by past researchers. As we all know, raw and acetylated sugarcane bagasse were already studied their sorbent properties to use in oil sorption by past researchers. Furthermore, we can see that the modification of the sorbents really improve the sorption capacity making both of the sorbents have greater capacity to absorb more oil from they're supposed to absorb. The modification of the sorbents really improve the sorption capacity making both of the sorbents have greater capacity to absorb more oil from they're supposed to absorb based on FTIR analysis. In both percentage removal of oil and oil sorption capacity, the optimum adsorption time is 15 minutes, while the optimum oil thickness is 10 ml. Based on the overall adsorption test results, sugarcane bagasse (non – wood) is a better oil sorbent than rubber wood (wood).

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